Identification of Chlorinated Nitrobenzene Residues in Mississippi River Fish

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Residues of lower chlorinated nitrobenzenes have been found at levels up to about 1 ppm in 8 samples of Mississippi River fish. Electron capture gas chromatography (EC/GC) was used for determination after extraction and cleanup using a procedure based on the AOAC multiresidue method for organochlorine and organophosphorus pesticides in nonfatty foods. The residues found included 2-, 3-, and 4-chloronitrobenzene and 2,3- and 3,4-dichloronitrobenzene; identity was confirmed by GC/mass spectrometry. GC retention times for 15 monochloro- through pentachloro-substituted nitrobenzene congeners were determined with OV-101 and mixed OV-101 + OV-210 columns at 130°C. In studies of the nonfatty food extraction and cleanup procedures of the AOAC method, recoveries of 15 chlorinated nitrobenzenes from spiked fish samples ranged from 68 to 116%. GC of cleaned up fish extract aliquots equivalent to 20 mg sample allowed quantitation of individual congeners at levels of about 0.025 and 0.005 ppm with ^{3}H and ^{63}Ni EC detectors, respectively. The contamination of Mississippi River fish with chlorinated nitrobenzenes appears to be localized in a 150 mile section of the river extending from St. Louis, MO, to Cape Girardeau, MO; no chlorinated nitrobenzenes (<0.005 ppm) were detected in Mississippi River fish caught above or below this region of the river or in fish from the lower Missouri River, which joins the Mississippi River near St. Louis.

Food and Drug Administration (FDA) personnel use the AOAC official multiresidue method for organochlorine and organophosphorus pesticides (secs. 29.001-29.018 (1)) to analyze foods for many potentially hazardous contaminants besides those for which the method has official status (2). Since 1976, FDA monitoring programs for pesticide and industrial chemical residues in foods have included analyses of selected food samples, mainly of domestic freshwater fish, for residues of electron-capturing industrial chemicals that are recovered in the 6% ethyl ether–petroleum ether eluate of the Florisil cleanup procedure (sec. 29.015 (1)), but are too volatile for electron capture gas chromatography (EC/GC) analysis at the operating conditions recommended in sec. 29.018 (1). EC/GC of these volatile compounds, called "early eluting industrial chemicals" because they elute from the OV-101 GC column before the residues usually determined by the method, is carried out with the OV-101 column temperature at 130°C instead of the recommended 200°C for pesticides. As part of an ongoing FDA program to identify new or previously unrecognized industrial chemical contaminants of foods, our laboratory investigates food samples that give unidentified analytical responses when monitored for early eluting industrial chemicals at FDA field laboratories.

In one of these investigations, monochloro- and dichloronitrobenzene residues were identified in a sample of Mississippi River buffalofish caught about 60 miles south of St. Louis, MO. The sample was first noted to yield an unidentified EC/GC response in an analysis for early eluting residues at the FDA Minneapolis District laboratory. When the analytical characteristics of the unknown compound were found to differ from those of the compounds listed in an FDA compilation of GC characteristics and AOAC method behavior data for volatile industrial chemicals, the sample was sent to this laboratory for further study. After the residues were tentatively identified as monochloro- and dichloronitrobenzene congeners by GC/mass spectrometry (MS), retention times and recoveries through the nonfatty food extraction and cleanup procedures of the AOAC method (1) were determined for 15 monochloro- through pentachloronitrobenzene congeners. Follow-up analyses of 12 additional fish samples from the Mississippi River and 6 fish samples from the last 300 miles of the Missouri River were performed. Chloronitrobenzenes were found at levels up to about 1 ppm in 7 samples caught in the Mississippi River near or below St. Louis. Residues found included 2-, 3-, and 4-chloronitrobenzene and 2,3- and 3,4-dichloronitrobenzene; their identities were confirmed by GC/MS comparisons with reference standards of the congeners.

Monochloronitrobenzenes have been reported as contaminants of river and drinking waters (3), but neither these compounds nor dichloronitrobenzenes have previously been reported as environmental contaminants of fish or other foods. Annual United States production of

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